

METHOD OF PRODUCTION OF DIELECTRIC CERAMIC COMPOSITION AND  
METHOD OF PRODUCTION OF ELECTRONIC DEVICE CONTAINING  
DIELECTRIC LAYERS

5 [0001]

**BACKGROUND OF THE INVENTION**

**1. Field of the Invention**

10 The present invention relates to a method of production of a dielectric ceramic composition and a method of production of an electronic device containing dielectric layers such as a multilayer ceramic capacitor.

[0002]

**2. Description of the Related Art**

15 A multilayer ceramic capacitor is broadly used as a compact, large capacity, high reliability electronic device. A large number are used in electrical equipment and electronics. In recent years, along with the reduction in size and improvement in performance of such equipment, increasingly tough demands are being made for further  
20 reduction of size, increase of capacity, lowering of price, and improvement of reliability of such multilayer ceramic capacitors.

[0003]

25 A multilayer ceramic capacitor is normally produced by stacking and firing a paste of internal electrodes and a slurry of a dielectric (paste) by the sheet method or printing method. In general, Pd or Pd alloy had been used for such internal electrodes, but Pd is high in price, so relatively inexpensive Ni or Ni alloy is now being used.  
30 When forming the internal electrodes by Ni or an Ni alloy, however, if firing in the atmosphere, there is the problem that the electrodes end up oxidizing. Therefore, in general, after the binder is removed, firing is performed at an oxygen partial pressure lower than the equilibrium oxygen  
35 partial pressure of Ni and NiO, then the dielectric layers

are reoxidized by heat treatment (Japanese Unexamined Patent Publication (Kokai) No. 3-113116 and Japanese Patent No. 2787746).

[0004]

5 If firing in a reducing atmosphere, however, the dielectric layers are reduced and the specific resistance ends up becoming smaller. Therefore, a reduction resistant dielectric material which is not reduced even if fired in a reducing atmosphere has been proposed (I. Burn et al., "High Resistivity BaTiO<sub>3</sub> Ceramics Sintered in CO-CO<sub>2</sub> Atmospheres", *J. Mater. Sci.*, 10, 633 (1975); Y. Sakabe et al., "High-Dielectric Constant Ceramics for Base Metal Monolithic Capacitors", *pn J. Appl. Phys.*, 20 Supple. 20-4, 147 (1981)).

15 [0005]

A multilayer ceramic capacitor using such reduction resistant dielectric materials, however, suffers from the problem of a short high temperature accelerated lifetime of the insulation resistance (IR) and a low reliability. Further, it suffers from the problem that the specific dielectric constant of the dielectric falls along with time. This is particularly remarkable under a DC electric field. If the thickness of the dielectric layers is reduced to make the multilayer ceramic capacitor smaller in size and larger in capacity, the strength of the electric field applied to the dielectric layers when applying a DC voltage becomes larger. Therefore, the change in the specific dielectric constant becomes remarkably larger.

[0006]

30 In the standard known as the X7R characteristic set in the EIA standard, the rate of change of the capacity is set within  $\pm 15\%$  between  $-55^{\circ}\text{C}$  to  $125^{\circ}\text{C}$  (reference temperature of  $25^{\circ}\text{C}$ ). As a dielectric material satisfying the X7R characteristic, for example, the BaTiO<sub>3</sub>+SrTiO<sub>3</sub>+MnO-based composition disclosed in Japanese Unexamined Patent

Publication (Kokai) No. 61-36170 is known. This composition, however, changes a large degree in capacity along with time under a DC electric field. For example, if a DC electric field of 50V is applied at 40°C for 1000 hours, the rate of change of the capacity ends up becoming about -10 to -30% or so and therefore the X7R characteristic can no longer be satisfied.

[0007]

Further, in the standard called the "B characteristic", that is, the temperature characteristic of the capacity (EIAJ standard), the rate of change is set to within ±10% between -25 to 85°C (reference temperature of 20°C).

[0008]

Further, as other reduction resistant dielectric ceramic compositions, the BaTiO<sub>3</sub>+MnO+MgO disclosed in Japanese Unexamined Patent Publication (Kokai) No. 57-71866, the (Ba<sub>1-x</sub>Sr<sub>x</sub>O)<sub>a</sub>Ti<sub>1-y</sub>Zr<sub>y</sub>O<sub>2</sub>+α((1-z)MnO+zCoO)+β((1-t)A<sub>2</sub>O<sub>5</sub>+tL<sub>2</sub>O<sub>3</sub>)+wSiO<sub>2</sub> (where A=Nb, Ta, V; L=Y or a rare earth element) disclosed in Japanese Unexamined Patent Publication (Kokai) No. 61-250905, the barium titanate adding Ba<sub>a</sub>Ca<sub>1-a</sub>SiO<sub>3</sub> disclosed in Japanese Unexamined Patent Publication (Kokai) No. 2-83256, etc. may be mentioned.

[0009]

However, even with these dielectric ceramic compositions, if the thickness of the dielectric layers is a superthin one of for example less than 4 μm, it is extremely difficult to satisfy all of the properties of the temperature characteristic of the capacity, the change in capacity along with time under a DC electric field, the accelerated lifetime of the insulation resistance, and the drop in capacity under a DC bias. For example, in the compositions disclosed in Japanese Unexamined Patent Publication (Kokai) No. 61-250905 and Japanese Unexamined Patent Publication (Kokai) No. 2-83256, the problem arises of a short accelerated lifetime of the insulation resistance

and a large drop in capacity under a DC bias.

[0010]

#### SUMMARY OF THE INVENTION

An object of the present invention is to provide a  
5 method of production for obtaining a multilayer ceramic  
capacitor or other electronic device containing dielectric  
layers able to satisfy all of the temperature  
characteristics of capacity, that is, the X7R characteristic  
(EIA standard) and B characteristic (EIAJ standard), even  
10 when the dielectric layers are superthin layers and having a  
small change in capacity along with time under a DC electric  
field, a long accelerated lifetime of the insulation  
resistance, and small drop in capacity under a DC bias.  
Another object of the present invention is to provide a  
15 method of production of a dielectric ceramic composition  
able to be suitably used as a dielectric layer of a  
multilayer ceramic capacitor or other electronic device  
containing dielectric layers having such superior  
properties.

[0011]

To achieve the first object, according to a first aspect  
of the present invention, there is provided a method of  
production of a dielectric ceramic composition having at  
least

25 a main component expressed by a formula  $Ba_mTiO_{2+n}$ ,  
wherein m is  $0.995 \leq m \leq 1.010$ , n is  $0.995 \leq n \leq 1.010$ , and the  
ratio of Ba and Ti is  $0.995 \leq Ba/Ti \leq 1.010$ ,

a first subcomponent containing at least one  
compound selected from MgO, CaO, BaO, SrO, and  $Cr_2O_3$ ,

30 a second subcomponent containing at least one  
compound selected from  $SiO_2$ , MO (where M is at least one  
element selected from Ba, Ca, Sr, and Mg),  $Li_2O$ , and  $B_2O_3$ ,

a third subcomponent containing at least one  
compound selected from  $V_2O_5$ ,  $MoO_3$ , and  $WO_3$ , and

35 a fourth subcomponent containing an oxide of R

(where R is at least one element selected from Y, Dy, Td, Gd, and Ho), wherein

the ratio of the subcomponents with respect to 100 moles of the main component is

- 5 first subcomponent: 0.1 to 3 moles,  
second subcomponent: 2 to 12 moles,  
third subcomponent: 0.01 to 3 moles,  
fourth subcomponent: 0.1 to 10.0 moles (where, the number of moles of the fourth subcomponent is a ratio of R alone),  
10

said method of producing the dielectric ceramic composition comprising the step of:

mixing in said main component at least part of other subcomponents except for said second subcomponent to prepare a pre-calcination powder,  
15

calcining the pre-calcination powder to prepare a calcined powder, and

mixing at least said second subcomponent in said calcined powder to obtain the dielectric ceramic composition having molar ratios of the subcomponents to the main component of the above ratios.  
20

[0012]

In the method of the present invention, preferably a dielectric ceramic composition further containing a fifth subcomponent containing MnO and having a ratio of the fifth subcomponent to 100 moles of the main component of 0.05 to 1.0 mole is obtained.  
25

[0013]

Preferably, a dielectric ceramic composition having a molar ratio of the third subcomponent to 100 moles of the main component of 0.01 to 0.1 mole, more preferably 0.01 to less than 0.1 mole, is obtained.  
30

[0014]

In the present invention, more preferably, the second subcomponent is expressed by  $(\text{Ba,Ca})_x\text{SiO}_{2+x}$  (where  $x=0.7$  to  
35

1.2). The second subcomponent is considered to function as a sintering aid.

When the second subcomponent has a composition expressed by  $(\text{Ba,Ca})_x\text{SiO}_{2+x}$  (where  $x=0.7$  to  $1.2$ ), the ratio of Ba and Ca in the second subcomponent may be any ratio. Inclusion of only one is also possible.

[0015]

Note that in the specification, the oxides comprising the main component and the subcomponents are expressed by stoichiiochemical compositions, but the states of oxidation of the oxides may also deviate from the stoichemical compositions. The above ratios of the subcomponents are found by conversion from the amounts of metals contained in the oxides comprising the subcomponents to the oxides of the above stoichiiochemical compositions. Further, as the powder materials of the dielectric ceramic composition, it is possible to use the above oxides or their mixtures or composite oxides, but it is also possible to suitably select and mix various compounds forming the above oxides or composite oxides upon firing, such as carbonates, oxalates, nitrates, hydroxides, and organic metal compounds.

In the present invention, a mean particle size of the main component is not particularly limited, but preferably is  $0.1$  to  $0.7 \mu\text{m}$ , more preferably  $0.2$  to  $0.7 \mu\text{m}$ .

[0016]

In the present invention, preferably, the pre-calcination powder is prepared so that the molar ratios of components contained in the pre-calcination powder  $(\text{Ba}+\text{metal element of the first subcomponent})/(\text{Ti}+\text{metal element of the fourth subcomponent})$  is less than  $1$ , or  $(\text{Ba}+\text{metal element of the fourth subcomponent})/(\text{Ti}+\text{metal element of the first subcomponent})$  is over  $1$ , and calcination is performed.

[0017]

In the present invention, preferably, the first subcomponent is always contained in the pre-calcination

powder when preparing the pre-calcination powder.

[0018]

In the present invention, when the pre-calcination powder contains the material of the fourth subcomponent, the calcination temperature is preferably 500°C to less than 1200°C, more preferably 600 to 900°C. Further, when the pre-calcination powder does not contain the material of the fourth subcomponent, the calcination temperature is preferably 600 to 1300°C, more preferably 900 to 1300°C, particularly preferably 1000 to 1200°C.

Note that the calcination may also be performed for a plurality of times.

[0019]

The calcined powder should have at least the second subcomponent mixed in it. If necessary, it is possible to further mix in at least one of the main component, first subcomponent, third subcomponent, fourth subcomponent, and fifth subcomponent in accordance with need. It is sufficient that the composition of the dielectric ceramic composition finally obtained become the above range.

[0020]

To achieve the second object, according to a second aspect of the present invention, there is provided a method of production of a multilayer ceramic capacitor comprised by alternately stacking interal electrodes comprised of Ni or Ni alloy and dielectric layers, where each of dielectric layers contains, in the molar ratios indicated,  $\text{BaTiO}_3$ : 100 moles, at least one of  $\text{MgO}$  and  $\text{CaO}$ : 0.1 to 3 moles,  $\text{MnO}$ : 0.05 to 1.0 mole,  $\text{Y}_2\text{O}_3$ : 0.1 to 5 moles,  $\text{V}_2\text{O}_5$ : 0.01 to 3 moles, and  $\text{Ba}_a\text{Ca}_{1-a}\text{SiO}_3$  (where the symbol (a) is a number from 0 to 1): 2 to 12 moles,

characterized by using at least 70 wt% of the material, which is premixed in  $\text{BaTiO}_3$  at least one of  $\text{MgO}$ ,  $\text{CaO}$  and a compound forming  $\text{MgO}$  or  $\text{CaO}$  upon heat treatment, and pre-calcined at a temperature of 900°C to 1300°C, with respect

to the entire dielectric material.

[0021]

To achieve the second object, according to a third aspect of the present invention, there is provided a method of production of a multilayer ceramic capacitor comprised by alternately stacking internal electrodes comprised of Ni or Ni alloy and dielectric layers, where each of dielectric layers contains, in the molar ratios indicated,  $\text{BaTiO}_3$ : 100 moles, at least one of  $\text{MgO}$  and  $\text{CaO}$ : 0.1 to 3 moles,  $\text{MnO}$ : 0.05 to 1.0 mole,  $\text{Y}_2\text{O}_3$ : 0.1 to 5 moles,  $\text{V}_2\text{O}_5$ : 0.01 to 3 moles, and  $\text{Ba}_a\text{Ca}_{1-a}\text{SiO}_3$  (where the symbol (a) is a number from 0 to 1): 2 to 12 moles,

characterized by using at least 70 wt% of the material, which is premixed in  $\text{BaTiO}_3$  at least one of  $\text{MgO}$ ,  $\text{CaO}$  and a compound forming  $\text{MgO}$  or  $\text{CaO}$  upon heat treatment,  $\text{MnO}$  or a compound forming  $\text{MnO}$  upon heat treatment,  $\text{Y}_2\text{O}_3$  or a compound forming  $\text{Y}_2\text{O}_3$  upon heat treatment, and  $\text{V}_2\text{O}_5$  or a compound forming  $\text{V}_2\text{O}_5$  upon heat treatment, and pre-calcined at a temperature of  $900^\circ\text{C}$  to  $1300^\circ\text{C}$ , with respect to the entire dielectric material.

[0022]

In the second and third aspects of the present invention, the molar ratio of the  $\text{V}_2\text{O}_5$  to 100 moles of the  $\text{BaTiO}_3$  is preferably 0.01 to 0.1 mole, more preferably 0.01 to less than 0.1 mole. Further, in the second and third aspects of the present invention, a mean particle size of the  $\text{BaTiO}_3$  is preferably 0.2 to  $0.7\ \mu\text{m}$ . Note that in the second and third aspects of the present invention, the number of moles of  $\text{Y}_2\text{O}_3$  is the number of moles of  $\text{Y}_2\text{O}_3$  not the number of moles of Y alone.

[0023]

In the method of production of a conventional dielectric ceramic composition, the  $\text{Ba}_m\text{TiO}_{2+n}$  and the additives are mixed once to prepare the mixed powder or dielectric paste of the dielectric ceramic composition. With the conventional



method, however, segregation of the additives (first to fifth subcomponents) etc. occurs in the dielectric ceramic composition after firing and variations end up occurring in the composition between crystals. Due to this segregation, the dielectric constant and the insulation resistance of the dielectric deteriorate.

[0024]

According to the present invention, by mixing in the main component at least one of the first subcomponent, third subcomponent, fourth subcomponent, and fifth subcomponent, and calcining, leaving aside the second subcomponent, it is possible to suppress variations in the composition between the crystal grains and as a result to suppress the precipitation of the segregation phase and control the size of the segregation phase. Therefore, according to the present invention, it is possible to produce a dielectric ceramic composition suitable for use for a multilayer ceramic capacitor or other electronic device including dielectric layers satisfying both the X7R characteristic and B characteristic, having little change in the capacity under a DC electric field along with time, having a long accelerated lifetime of the insulation resistance, having a small drop in capacity under a DC electric field, and superior in reliability. This was first discovered by the present inventors.

[0025]

Further, the dielectric ceramic composition obtained by the method of production of the present invention does not contain an element like Pb, Bi, or Zn which evaporates and scatters, so can be fired even in a reducing atmosphere. Therefore, it becomes possible to use a base metal such as Ni or an Ni alloy as the internal electrodes and possible to reduce the cost.

[0026]

Further, the dielectric ceramic composition obtained by

the method of production according to the present invention satisfies the X7R characteristic and the B characteristic, has little deterioration of the aging characteristic of the capacity and insulation resistance due to application of a DC electric field, and is superior in reliability even in firing under a reducing atmosphere. Therefore, the method of the present invention can be expected to be effective as a technique for suppressing deterioration of the rate of change of temperature of the high temperature region accompanying the increased thickness of multilayer capacitors.

[0027]

Further, the dielectric ceramic composition obtained by the method of production does not contain Pb, Bi, or other substance, so a product with a small detrimental impact on the environment due to dumping, disposal, etc. after use can be provided.

[0028]

Further, with the method of production according to the present invention, it is possible to realize a dielectric ceramic composition of a uniform composition with little different phases formed by precipitation of the additives and possible to improve the dielectric constant and insulation resistance of the dielectric ceramic composition.

Further, with the method of production of the present invention, it is possible to prevent structural defects occurring incidentally, so it is possible to provide a multilayer ceramic capacitor having a high reliability.

[0029]

Since it is possible to suppress precipitation of different phases without changing the additive composition, it is possible to easily produce a multilayer ceramic capacitor or other electronic device containing dielectric layers having a capacity-temperature characteristic satisfying the X7R characteristic and B characteristic.

[0030]

In particular, in the present invention, by making the ratio of the third subcomponent to 100 moles of the main component preferably 0.01 to 0.1 mole, more preferably 0.01 to less than 0.1 mole, the insulation resistance (IR), CR product (product of the dielectric constant and the insulation resistance), breakdown voltage (VB) characteristic, and resistance to drop in capacity under a DC bias (DC-Bias characteristic) are improved.

The present disclosure relates to subject matter contained in Japanese Patent Application No. 2000-250156, filed on August 21, 2000, the disclosure of which is expressly incorporated herein by reference in its entirety.

[0031]

#### BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects and features of the present invention will be explained in further detail with reference to the attached drawing, FIG. 1, which is a sectional view of a multilayer ceramic capacitor according to an embodiment of the present invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Next, the present invention will be explained based on the embodiment shown in the drawing.

[0032]

#### Multilayer Ceramic Capacitor

Before explaining the method of production of a dielectric ceramic composition according to the present invention, an explanation will be made of a multilayer ceramic capacitor.

As shown in FIG. 1, a multilayer ceramic capacitor 1 according to an embodiment of the present invention has a capacitor device body 10 of a configuration of dielectric layers 2 and internal electrode layers 3 stacked alternately. At the two ends of the capacitor device body 10 are formed a pair of external electrodes 4 conductive with

the internal electrode layers 3 alternately arranged inside the device body 10. The shape of the capacitor device body 10 is not particularly limited, but normally is made a parallelopiped. Further, the dimensions are not particularly limited and may be made suitable dimensions in accordance with the application. Usually, however, they are (0.6 to 5.6 mm, preferably 0.6 to 3.2 mm) x (0.3 to 5.0 mm, preferably 0.3 to 1.6 mm) x (0.3 to 1.9 mm, preferably 0.3 to 1.6 mm).

[0033]

The internal electrode layers 3 are stacked so that end faces thereof alternately protrude out to the surfaces of the two opposing ends of the capacitor device body 10. The pair of external electrodes 4 are formed at the two ends of the capacitor device body 10 and are connected to the exposed end faces of the alternately arranged internal electrode layers 3 to form a capacitor circuit.

[0034]

#### Dielectric Layers 2

Each of the dielectric layers 2 contains the dielectric ceramic composition obtained by the method of production of the present invention.

The dielectric ceramic composition obtained by the method of production of the present invention is comprised of a dielectric ceramic composition having at least

a main component expressed by the formula  $Ba_mTiO_{2+n}$  wherein m in the formula is  $0.995 \leq m \leq 1.010$ , n is  $0.995 \leq n \leq 1.010$ , and the ratio of Ba and Ti is  $0.995 \leq Ba/Ti \leq 1.010$ ,

a first subcomponent including at least one compound selected from MgO, CaO, BaO, SrO, and  $Cr_2O_3$ ,

a second subcomponent including at least one compound selected from  $SiO_2$ , MO (where M is at least one type of element selected from Ba, Ca, Sr, and Mg),  $Li_2O$ , and  $B_2O_3$ ,

a third subcomponent including at least one compound selected from  $V_2O_5$ ,  $MoO_3$ , and  $WO_3$ , and

a fourth subcomponent including an oxide of R (wherein R is at least one element selected from Y, Dy, Tb, Gd, and Ho).

[0035]

5 The ratios of the subcomponents to the main component are, with respect to 100 moles of the main component,

First subcomponent: 0.1 to 3 moles,

Second subcomponent: 2 to 12 moles,

Third subcomponent: 0.01 to 3 moles,

10 Fourth subcomponent: 0.1 to 10.0 moles,

preferably

First subcomponent: 0.5 to 2.5 moles,

Second subcomponent: 2.0 to 5.0 moles,

15 Third subcomponent: 0.01 to 0.1 mole (0.01 to less than 0.1 mole),

Fourth subcomponent: 0.5 to 5.0 moles.

[0036]

Note that the ratio of the fourth subcomponent is the molar ratio of R alone, not the molar ratio of the R oxide. That is, this means that, when using for example an oxide of Y as the fourth subcomponent, the ratio of  $Y_2O_3$  is not 1 mole, but the ratio of Y is 1 mole.

[0037]

25 In this specification, the oxides comprising the main component and the subcomponents are expressed by stoichiochemical compositions, but the states of oxidation of the oxides may also deviate from the stoichiochemical compositions. The above ratios of the subcomponents are found by conversion from the amounts of metals contained in the oxides comprising the subcomponents to the oxides of the 30 above stoichiochemical compositions. Further, as the powder materials of the dielectric ceramic composition, it is possible to use the above oxides or their mixtures or composite oxides, but it is also possible to suitably select 35 and mix various compounds giving the above oxides or

composite oxides upon firing, such as carbonates, oxalates, nitrates, hydroxides, and organic metal compounds.

[0038]

5 The reasons for limitation of the contents of the subcomponents are as follows:

If the content of the first subcomponent ( $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{BaO}$ ,  $\text{SrO}$ , and  $\text{Cr}_2\text{O}_3$ ) is too small, the effect of suppression of the drop in capacity under a DC bias tends to become insufficient. On the other hand, if the content is too large, the drop in the dielectric constant tends to become remarkable and the accelerated lifetime of the insulation resistance tends to become shorter. Note that the ratios of the oxides in the first subcomponent may be any ratios.

[0039]

15 If the content of the second subcomponent is too small, the sinterability becomes poor, the accelerated lifetime of the insulation resistance becomes short, and the temperature characteristic of the capacity no longer satisfies the standard of the X7R characteristic. On the other hand, if the content is too great, the dielectric constant becomes low, the capacity falls, and the accelerated lifetime of the insulation resistance also becomes shorter.

[0040]

25 The second subcomponent mainly acts as a sintering aid, but also has the effect of reducing the defect rate of the initial insulation resistance when making the dielectric layers thinner.

30 Preferably, the second subcomponent is expressed by  $(\text{Ba,Ca})_x\text{SiO}_{2+x}$  (where,  $x = 0.7$  to  $1.2$ ). The  $\text{BaO}$  and the  $\text{CaO}$  in the  $[(\text{Ba,Ca})_x\text{SiO}_{2+x}]$  of a more preferable embodiment of the second subcomponent are also contained in the first subcomponent, but the composite oxide  $(\text{Ba,Ca})_x\text{SiO}_{2+x}$  has a low melting point, so the reactivity with respect to the main component is good. In the present invention, it is preferable to add  $\text{BaO}$  and/or  $\text{CaO}$  as the above composite

oxides. The  $x$  in the  $(\text{Ba,Ca})_x\text{SiO}_{2+x}$  of the more preferable embodiment of the second subcomponent is preferably 0.7 to 1.2, more preferably 0.8 to 1.1. If  $x$  is too small, that is, if  $\text{SiO}_2$  is too great, it reacts with the main component

5  $\text{BaTiO}_3$  and ends up causing the dielectric property to deteriorate. On the other hand, if  $x$  is too large, the melting point becomes higher and the sinterability is deteriorated, so this is not preferred. Note that the ratio of Ba and Ca may be any ratio. It is also possible to  
10 include only one.

[0041]

If the content of the third subcomponent ( $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$ , or  $\text{WO}_3$ ) is too small, the IR lifetime under a DC electric field falls and the temperature characteristic of the capacity  
15 tends to no longer satisfy the standard of the X7R characteristic. On the other hand, if the content is too large, the initial insulation resistance tends to become lower and the CR product also tends to become lower. Note that the ratios of the oxides in the third subcomponent may  
20 be any ratios.

[0042]

If the content of the fourth subcomponent (R oxide) is too small, the accelerated lifetime of the insulation resistance tends to become shorter. On the other hand, if  
25 the content is too large, the sinterability tends to deteriorate. Among these, from the viewpoint of satisfying the X7R characteristic, among the fourth subcomponents, a Y oxide, Dy oxide, or Ho oxide is preferable. In particular, since the effect of improving the properties is high and the  
30 cost is low, a Y oxide is preferable.

[0043]

The dielectric ceramic composition of the present invention may also contain, in accordance with need,  $\text{MnO}$  as  
35 a fifth subcomponent. The fifth subcomponent exhibits the effect of promotion of sintering and the effect of reduction

of the dielectric loss ( $\tan\delta$ ). To sufficiently obtain such an effect, it is preferable that the ratio of the fifth subcomponent to 100 moles of the main component be at least 0.05 mole. If the content of the fifth subcomponent is too large, however, a detrimental effect is given to the capacity-temperature characteristic, so the content is preferably made not more than 1.0 mole.

[0044]

Further, the dielectric ceramic composition of the present invention may also contain, in addition to the above oxides,  $\text{Al}_2\text{O}_3$ .  $\text{Al}_2\text{O}_3$  does not have much of an effect on the capacity-temperature characteristic and has the effect of improvement of the sinterability, insulation resistance, and accelerated lifetime (IR lifetime) of the insulation resistance. If the content of the  $\text{Al}_2\text{O}_3$  is too large, however, the sinterability deteriorates and the IR falls, so the  $\text{Al}_2\text{O}_3$  is preferably not more than 1 mole with respect to 100 moles of the main component, preferably not more than 1 mole of the dielectric ceramic composition as a whole.

[0045]

Note that when at least one of Sr, Zr, and Sn replaces the Ba or Ti in the main component forming the perovskite structure, the Curie temperature shifts to the low temperature side, so the capacity-temperature characteristic over  $125^\circ\text{C}$  deteriorates. Therefore, it is preferable not to use  $\text{Ba}_m\text{TiO}_{2+n}$  containing these elements [for example,  $(\text{Ba},\text{Sr})\text{TiO}_3$ ] as the main component. However, there is no particular problem at the level of content as an impurity (not more than about 0.1 mol% of the dielectric ceramic composition as a whole).

[0046]

The mean particle size of the dielectric ceramic composition of the present invention is not particularly limited and may be suitably determined in accordance with the thickness of the dielectric layer, for example, from the



range of 0.1 to 3.0  $\mu\text{m}$ , preferably 0.1 to 0.7  $\mu\text{m}$ . The capacity-temperature characteristic deteriorates the thinner the dielectric layers and tends to deteriorate the smaller the mean crystal grain size. Therefore, the dielectric ceramic composition of the present invention is particularly effective when it is necessary to reduce the mean crystal grain size, specifically when the mean crystal grain size is 0.1 to 0.5  $\mu\text{m}$ . Further, if the mean crystal grain size is reduced, the IR lifetime becomes longer and the change of the capacity along with time under a DC bias becomes smaller, so from this viewpoint as well, the mean crystal grain size is preferably small as explained above.

[0047]

A dielectric layer of the present invention is configured by grains, grain boundaries, and grain boundary phases. Further, it may also be configured by a composition having a so-called core-shell structure.

[0048]

Note that the thickness, number of layers, and other various conditions of the dielectric layers comprised of the dielectric ceramic composition of the present invention may be suitably determined in accordance with the object and application. For example, the thickness of the dielectric layers is normally not more than 50  $\mu\text{m}$  per layer, particularly not more than 10  $\mu\text{m}$ . The lower limit of the thickness is usually about 1  $\mu\text{m}$ . The dielectric ceramic composition of the present invention is effective in improving the capacity-temperature characteristic of a multilayer ceramic capacitor having such thinner dielectric layers. Note that the number of the dielectric layers is normally 2 to 400, preferably 10 to 400 or so.

[0049]

The multilayer ceramic capacitor used in the dielectric ceramic composition of the present invention is suitably used as an electronic device for equipment used in an

environment of  $-55^{\circ}\text{C}$  to  $+125^{\circ}\text{C}$ . Further, in this temperature range, the capacity-temperature characteristic can satisfy the X7R characteristic of the EIA standard (within  $\Delta C = \pm 15\%$  at  $55$  to  $125^{\circ}\text{C}$ ) and simultaneously satisfy the B

5 characteristic of the EIAJ standard [rate of change of capacity within  $\pm 10\%$  at  $-25$  to  $85^{\circ}\text{C}$  (reference temperature  $20^{\circ}\text{C}$ )].

[0050]

10 In the multilayer ceramic capacitor, an AC electrical field of normally at least  $0.02\text{V}/\mu\text{m}$ , in particular at least  $0.2\text{V}/\mu\text{m}$ , further at least  $0.5\text{V}/\mu\text{m}$ , and in general not more than about  $5\text{V}/\mu\text{m}$ , and, superposed on this, a DC electrical field of not more than  $5\text{V}/\mu\text{m}$  are applied to the dielectric layers, but even if such electrical fields are applied, the  
15 temperature characteristic of the capacity is extremely stable.

[0051]

#### Internal Electrode Layers 3

20 The electroconductive material contained in the internal electrode layers 3 is not particularly limited, but a base metal may be used since the material constituting the dielectric layers 2 has resistance to reduction. As the base metal used as the electroconductive material, Ni or an Ni alloy is preferable. As the Ni alloy, an alloy of at least  
25 one type of element selected from Mn, Cr, Co, and Al with Ni is preferable. The content of the Ni in the alloy is preferably not less than 95 wt%.

Note that the Ni or Ni alloy may contain P and other various types of trace components in amounts of not more  
30 than 0.1 wt% or so.

The thickness of the internal electrode layers may be suitably determined in accordance with the application etc., but is usually  $0.5$  to  $5\ \mu\text{m}$ , preferably  $0.5$  to  $2.5\ \mu\text{m}$ , more preferably  $1$  to  $2\ \mu\text{m}$  or so.

35 [0052]

#### External Electrodes 4

The electroconductive material contained in the external electrodes 4 is not particularly limited, but in the present invention, an inexpensive Ni, Cu, or alloys of the same are used.

The thickness of the external electrodes may be suitably determined in accordance with the application etc., but is usually 10 to 100  $\mu\text{m}$  or so.

[0053]

#### 10 Method of Manufacturing Multilayer Ceramic Capacitor

The multilayer ceramic capacitor produced using the method of production of a dielectric ceramic composition according to the present invention is produced by preparing a green chip using the usual printing method or sheet method which uses pastes, firing the green chip, then printing or transferring the external electrodes and firing. The method of production will be explained in detail below.

[0054]

First, the dielectric ceramic composition powder contained in the dielectric layer paste is prepared. The powder of  $\text{BaTiO}_3$  in the dielectric ceramic composition powder includes not only a powder obtained normally by mixing the materials, then calcining and pulverizing them, that is, the solid phase method, but also powder obtained by the oxalate method or the hydrothermal synthesis method or other so-called liquid phase methods.

[0055]

In the present invention, calcination is performed before obtaining the dielectric ceramic composition powder of the above composition. That is, a pre-calcination powder is prepared by mixing and drying at least one of the main component ( $\text{Ba}_m\text{TiO}_{2+n}$ ) and the first subcomponent (for example, MgO or CaO or a compound forming MgO or CaO upon heat treatment), the third subcomponent (for example,  $\text{V}_2\text{O}_5$  or a compound forming  $\text{V}_2\text{O}_5$  upon heat treatment), the fourth

subcomponent (for example,  $Y_2O_3$  or a compound forming  $Y_2O_3$  upon heat treatment), and the fifth subcomponent (for example,  $MnO$  or a compound forming  $MnO$  upon heat treatment), leaving aside the second subcomponent (for example,

5  $(Ba,Ca)_xSiO_{2+x}$ ).

[0056]

Note that as compounds forming  $MgO$  or  $CaO$  upon heat treatment,  $MgCO_3$ ,  $MgCl_2$ ,  $MgSO_4$ ,  $Mg(NO_3)_2$ ,  $Mg(OH)_2$ ,  $(MgCO_3)_4Mg(OH)_2$ ,  $CaCO_3$ ,  $CaCl_2$ ,  $CaSO_4$ ,  $Ca(NO_3)_2$ ,  $Mg$  alkoxide,  $Ca$  alkoxide, etc. and hydrates of the same may be illustrated. Further, as compounds forming  $MnO$  upon heat treatment,  $MnCO_3$ ,  $MnCl_2$ ,  $MnSO_4$ ,  $Mn(NO_3)_2$ , and hydrates of the same may be illustrated. Further, as compounds forming  $Y_2O_3$  upon heat treatment,  $YCl_3$ ,  $Y_2(SO_4)_3$ ,  $Y(NO_3)_3$ ,  $Y(CH_3COO)_3$ ,  $Y$  alkoxide, and hydrates of the same may be illustrated. Further, as compounds forming  $V_2O_5$  upon heat treatment,  $VCl_5$ ,  $V_2(SO_4)_5$ ,  $V(NO_3)_5$ , etc. or hydrates of the same may be illustrated.

[0057]

The pre-calcination powder is calcined in the following way. The calcination conditions are not particularly limited, but preferably the calcination is performed under the conditions shown below:

Rate of temperature rise: 50 to 400°C/hour, in particular 100 to 300°C/hour

Holding temperature: 500 to 1300°C, preferably 500°C to less than 1200°C

Temperature holding time: 0.5 hour to 6 hours, in particular 1 to 3 hours

Atmosphere: Air and nitrogen

[0058]

The calcined powder is roughly pulverized by an alumina roll etc., then at least the second subcomponent (for example,  $(Ba,Ca)_xSiO_{2+x}$ ) is added, then, in accordance with need, the remaining additives are added to prepare the mixed powder of the final composition. Next, the mixed powder is

mixed by a ball mill etc. and dried according to need to obtain a dielectric ceramic composition powder having the composition of the present invention.

[0059]

5 The molar ratios of the components in the calcined powder are not particularly limited, but preferably satisfy the following relation. That is, it is preferable that (Ba+metal element of first subcomponent)/(Ti+metal element of fourth subcomponent) be less than 1 and that (Ba+metal  
10 element of fourth subcomponent)/(Ti+metal element of first subcomponent) be over 1. If in this range, the accelerated lifetime of the insulation resistance is particularly improved.

[0060]

15 Further, the calcined powder preferably always contains the first subcomponent. The calcined powder preferably contain 30 wt%, more preferably 50 wt%, of the first subcomponent when the total weight of the first subcomponent in the final composition powder is 100 wt%.

[0061]

20 The calcined powder is mixed with the later added components in an amount of preferably at least 60 wt%, more preferably at least 70 wt%, particularly preferably at least 80 wt%, with respect to the finally obtained dielectric  
25 ceramic composition powder as 100 wt%. If the ratio of the calcined powder is too small, the effect of the present invention tends to become small.

[0062]

30 Next, the finally obtained dielectric ceramic composition powder is made to a coating to prepare a dielectric layer paste. The dielectric layer paste may be an organic-based coating obtained by kneading the dielectric ceramic composition powder with an organic vehicle or may be a water-based coating.

35 [0063]

In the state before coating, the particle size of the dielectric ceramic composition powder is normally a mean particle size of 0.1 to 3  $\mu\text{m}$ , preferably 0.1 to 0.7  $\mu\text{m}$  or so.

5 [0064]

The organic vehicle is comprised of a binder dissolved in an organic solvent. The binder used for the organic vehicle is not particularly limited, but may be suitably selected from ethyl cellulose, polyvinyl butyrate, and other  
10 ordinary types of binders. Further, the organic solvent used is also not particularly limited and may be suitably selected from terpeneol, butyl carbitol, acetone, toluene, and other organic solvents in accordance with the printing method, sheet method, or other method of use.

15 [0065]

Further, when the dielectric layer paste is made a water-based coating, if it sufficient to knead a water-based vehicle comprised of a water-soluble binder, dispersant, etc. dissolved in water with the dielectric material. The  
20 water-soluble binder used in the organic vehicle is not particularly limited. For example, a polyvinyl alcohol, cellulose, water-based acrylic resin, etc. may be used.

[0066]

The internal electrode layer paste is prepared by  
25 kneading the electroconductive material comprised of the above various types of electroconductive metals and alloys or various types of oxides forming the above electroconductive materials after firing, an organometallic compound, resinate, etc. (electroconductive material)  
30 together with the above organic vehicle. The electroconductive material in the paste etc. is not particularly limited in shape. Balls, flakes, etc. may be mentioned. Further, these shapes may also be mixed together.

The external electrode paste is prepared in the same way  
35 as the internal electrode paste.

[0067]

The content of the organic vehicle in the above pastes is not particularly limited and may fall within the usual content, for example, the binder may be contained in an  
5 amount of 1 to 5 wt% or so and the solvent 10 to 50 wt% or so. Further, the pastes may include, in accordance with need, various types of additives selected from dispersants, plasticizers, dielectrics, insulators, etc. The total  
10 content of these auxiliary additives is preferably not more than 10 wt%.

[0068]

Note that as the plasticizer, for example, polyethylene glycol, a phthalic acid ester (for example, dioctyl  
15 phthalate, dibutyl phthalate), etc. may be used. Further, as the dispersant, for example, oleic acid, a rosin, glyceryl, octadecylamine, an oleic acid ethyl, a mencedene oil, etc. may be used.

[0069]

In particular, when preparing a dielectric layer paste (slurry), the content of the dielectric ceramic composition  
20 powder in the paste is preferably made about 50 to 80 wt% with respect to the paste as a whole, while the content of the binder is preferably made 2 to 5 wt%, the plasticizer 0.1 to 5 wt%, the dispersant 0.1 to 5 wt%, and the solvent  
25 20 to 50 wt% or so.

[0070]

When using the printing method, the dielectric layer paste and the internal electrode layer paste are printed on a substrate of PET etc., cut into a predetermined shape,  
30 then peeled from the substrate to obtain a green chip.

[0071]

Further, when using the sheet method, a green sheet is formed using the dielectric layer paste, the internal electrode layer paste is printed on this, then these sheets  
35 are stacked to form the green chip.

[0072]

Before firing, the green chip is processed to remove the binder. The processing for removing the binder may be performed under ordinary conditions, but particularly preferably is performed under the following conditions when using a base metal such as Ni or an Ni alloy for the electroconductive material of the internal electrode layers:

Rate of temperature rise: 50 to 300°C/hour, in particular 10 to 100°C/hour

Holding temperature: 180 to 400°C, in particular 200 to 300°C

Temperature holding time: 0.5 hour to 24 hours, in particular 5 to 20 hours

Atmosphere: Air

[0073]

The atmosphere when firing the green chip may be suitably determined in accordance with the type of the electroconductive material in the internal electrode layer paste, but when using a base metal such as Ni or an Ni alloy as the electroconductive material, the oxygen partial pressure in the firing atmosphere is preferably  $10^{-7}$  to  $10^{-13}$  atm, more preferably  $10^{-10}$  to  $10^{-12}$ . If the oxygen partial pressure is less than that range, the electroconductive material of the internal electrode layers is abnormally sintered and sometimes ends up breaking. Further, if the oxygen partial pressure is over that range, the internal electrode layers tend to oxidize.

[0074]

Further, the holding temperature at the time of firing is preferably 1100 to 1400°C, more preferably 1150 to 1400°C, still more preferably 1200 to 1300°C. If the holding temperature is less than that range, the densification becomes insufficient, while if over that range, the electrodes break due to abnormal sintering of the internal electrode layers, the capacity-temperature characteristic



deteriorates due to diffusion of the materials making up the internal electrode layers, and the dielectric ceramic composition becomes easily reducible.

[0075]

5 Preferably, the various conditions at the time of firing other than the above conditions are selected from the following range:

Rate of temperature rise: 100 to 900°C/hour, in particular 200 to 900°C/hour

10 Temperature holding time: 0.5 hour to 8 hours, in particular 1 to 3 hours

Cooling rate: 50 to 500°C/hour, in particular 200 to 300°C/hour

15 Note that the firing atmosphere is preferably made a reducing atmosphere. As the atmospheric gas, for example, it is preferable to use a wet mixed gas of  $N_2$  and  $H_2$ .

[0076]

20 When firing in a reducing atmosphere, it is preferable to anneal the capacitor device body. The annealing is processing for reoxidizing the dielectric layers and enables the IR lifetime to be remarkably prolonged, so improves the reliability.

[0077]

25 The oxygen partial pressure in the annealing atmosphere is preferably made  $10^{-4}$  to  $10^{-7}$  atm. If the oxygen partial pressure is less than the above range, the reoxidation of the dielectric layers is difficult, while if over the above range, the internal electrode layers tend to oxidize.

[0078]

30 The holding temperature at the time of annealing is preferably made not more than 1200°C, particularly 500 to 1200°C. If the holding temperature is less than the above range, the oxidation of the dielectric layers becomes insufficient, so the IR is low or the IR lifetime easily  
35 becomes shortened. On the other hand, if the holding

temperature is over the above range, not only do the internal electrode layers oxidize and the capacity fall, but also the internal electrode layers end up reacting with the dielectric material resulting in a susceptibility to deterioration of the capacity-temperature characteristic, a drop in the IR, and a drop in the IR lifetime. Note that the annealing may also be comprised of a temperature raising process and a temperature lowering process. That is, the temperature holding time may also be made zero. In this case, the holding temperature is synonymous with the maximum temperature.

[0079]

The various conditions at the time of annealing other than the above conditions are preferably selected from the following ranges:

Temperature holding time: 0.5 hour to 12 hours, in particular 6 to 10 hours

Cooling rate: 50 to 600°C/hour, in particular 100 to 300°C/hour

Note that the atmospheric gas is preferably wet N<sub>2</sub> gas etc.

[0080]

In the above processing to remove the solvent, firing, and annealing, the N<sub>2</sub> gas or the mixed gas etc. may be wet by for example using a wetter etc. In this case, the water temperature is preferably made 5 to 75°C or so.

[0081]

The processing to remove the solvent, firing, and annealing may be performed continuously or independently. If these are performed continuously, it is preferable to perform the processing to remove the binder, then change the atmosphere without cooling, then fire by raising the temperature up to the holding temperature at the time of firing, then cool, change the atmosphere when reaching the holding temperature for annealing, and anneal. On the other

hand, when performing these independently, at the time of firing, preferably the temperature is raised to the holding temperature of the time of processing to remove the binder in an N<sub>2</sub> gas or a wet N<sub>2</sub> gas atmosphere, then the atmosphere is changed and the temperature continued to be raised, then preferably the temperature is lowered to the holding temperature of the time of annealing, then the atmosphere is changed again to an N<sub>2</sub> gas or wet N<sub>2</sub> gas atmosphere and the cooling continued. Further, at the time of annealing, it is also possible to raise the temperature to the holding temperature in an N<sub>2</sub> gas atmosphere, then change the atmosphere or conduct the entire annealing process in a wet N<sub>2</sub> gas atmosphere.

[0082]

The thus obtained capacitor device body is, for example, end polished using barrel polishing or sandblasting etc., then printed or transferred with an external electrode paste and fired to form the external electrodes 4. The firing conditions of the external electrode paste are for example preferably 600 to 800°C for 10 minutes to 1 hour or so in a wet mixed gas of nitrogen and hydrogen. Further, in accordance with need, the surfaces of the external electrodes 4 may be formed with a covering layer by plating etc.

[0083]

The thus produced multilayer ceramic capacitor of the present invention has a capacity-temperature characteristic satisfying the X7R characteristic of the EIA standard and satisfying the B characteristic of the EIAJ standard even when the thickness of the dielectric layers is a superthin one of not more than 4 μm. Further, the multilayer ceramic capacitor of the present invention has a small change of the capacity over time under a DC electric field, a long accelerated lifetime of the insulation resistance, and a small drop in capacity under a DC bias.

[0084]

The thus produced multilayer ceramic capacitor of the present invention is mounted by soldering it onto a printed circuit board for use in various types of electronic equipment.

[0085]

Note that the present invention is not limited to the above embodiment and may be modified in various ways within the scope of the invention.

For example, the dielectric ceramic composition obtained by the method of production of the present invention is not used only for a multilayer ceramic capacitor and may be used for other electronic devices formed with dielectric layers as well.

[0086]

Below, the present invention will be explained in further detail with reference to more detailed examples, but the present invention is not limited to these examples.

[0087]

#### Example 1

Samples A1 to A10 of multilayer ceramic capacitors were prepared by the following routine:

First, the following pastes were prepared.

[0088]

#### Dielectric Layer Paste

First, the main component material and the subcomponent materials were prepared. As the main component material,  $\text{BaTiO}_3$  of a particle size of 0.2 to 0.7  $\mu\text{m}$  obtained by the hydrothermal synthesis method was used. For the  $\text{MgO}$  and the  $\text{MnO}$  materials, carbonates were used, while for the other subcomponent materials, oxides were used. As the magnesium carbonate used as the material of  $\text{MgO}$ ,  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$  was used. Further, as the carbonate used as the material of the  $\text{MnO}$ ,  $\text{MnCO}_3$  was used.

[0089]

Further, as the material of the second subcomponent,  $(\text{Ba}_{0.6}\text{Ca}_{0.4})\text{SiO}_3$  was used. Note that  $(\text{Ba}_{0.6}\text{Ca}_{0.4})\text{SiO}_3$  was produced by wet mixing  $\text{BaCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{SiO}_2$  by a ball mill for 16 hours, drying the result, then firing at  $1150^\circ\text{C}$  in the air and then further wet pulverizing the result by a ball mill for 100 hours.

[0090]

First, the main component,  $\text{BaTiO}_3$ , and the material of the first subcomponent, magnesium carbonate, were mixed and dried to prepare a pre-calcination powder. As shown in Table 1, the pre-calcination powder contained 2.1 moles of magnesium carbonate, converted to  $\text{MgO}$ , with respect to 100 moles of  $\text{BaTiO}_3$ . Further, when examining the molar ratio of specific components in the pre-calcination powder of  $(\text{Ba} + \text{metal element Mg in the first subcomponent}) / (\text{Ti} + \text{metal element Y in the fourth subcomponent})$ , as shown in Table 1, it was 1.021. Further, when examining the molar ratio of  $(\text{Ba} + \text{metal element Y in the fourth subcomponent}) / (\text{Ti} + \text{metal element Mg in the first subcomponent})$ , as shown in Table 1, it was 0.9794.

[0091]

Next, the pre-calcination powder was calcined. The calcination conditions were as follows:

Rate of temperature rise:  $300^\circ\text{C}/\text{hours}$ ,

Holding temperature (T1 in Table 1):  $500$  to  $1350^\circ\text{C}$

Temperature holding time: 3 hours

Atmosphere: Air

[0092]

The material obtained by the calcination was pulverized by a pulverizer for 1 hour to obtain a calcined powder, then as shown in Table 2, 3.0 moles of  $(\text{Ba}_{0.6}\text{Ca}_{0.4})\text{SiO}_3$ , 0.375 mole of  $\text{MnCO}_3$ , 0.01 mole of  $\text{V}_2\text{O}_5$ , and 2.1 mole of  $\text{Y}_2\text{O}_3$  (number of moles of Y: 4.2 moles, same below) were added to the calcined powder, wet mixed by a zirconia ball mill for 16 hours, then dried to obtain the dielectric ceramic

composition powder of the final composition.

[0093]

100 parts by weight of the thus obtained dielectric ceramic composition powder, 4.8 parts by weight of acrylic resin, 40 parts by weight of methylene chloride, 20 parts by weight of ethyl acetate, 6 parts by weight of mineral spirits, and 4 parts by weight of acetate were mixed by a ball mill for 16 hours to make a paste.

[0094]

10 Internal Electrode Layer Paste

44.6 parts by weight of Ni particles of a mean particle size of 0.4  $\mu\text{m}$ , 52.0 parts by weight of terpineol, 3.0 parts by weight of ethyl cellulose, and 0.4 part by weight of benzotriazole were kneaded by a triple roll to make a paste.

15 [0095]

External Electrode Layer Paste

100 parts by weight of Cu particles of a mean particle size of 2  $\mu\text{m}$ , 35 parts by weight of an organic vehicle (8 parts by weight of ethyl cellulose resin dissolved in 92 parts by weight of butyl carbitol), and 7 parts by weight of butyl carbitol were kneaded to make a paste.

20 [0096]

Preparation of Green Chip

A green sheet of a thickness of 5  $\mu\text{m}$  was formed on a PET film using the above dielectric layer paste. The internal electrode paste was printed on the surface of the green sheet, then the sheet was peeled off from the PET film. Next, four layers of the green sheet printed with the internal electrode layer paste were stacked with several protective green sheets (sheets not printed with internal electrode layer paste) in between them, then pressed under conditions of 120°C and 15 Pa to obtain a green chip.

30 [0097]

Firing

35 First, the green chip was cut to a predetermined size,

then processed to remove the binder, fired, and annealed under the following conditions, then formed with external electrodes to obtain Samples A1 to A10 of multilayer ceramic capacitors of the configuration shown in FIG. 1.

5 [0098]

Conditions of Processing to Remove Binder

Rate of temperature rise: 15°C/hour

Holding temperature: 280°C

Temperature holding time: 8 hours

10 Atmosphere: Air

[0099]

Firing Conditions

Rate of temperature rise: 200°C/hours

Holding temperature: 1270°C

15 Temperature holding time: 2 hours

Cooling rate: 300°C/hour

Atmosphere: Wet N<sub>2</sub>+H<sub>2</sub> mixed gas

Oxygen partial pressure: 10<sup>-12</sup> atm

[0100]

20 Annealing Conditions

Holding temperature: 1000°C

Temperature holding time: 3 hours

Cooling rate: 300°C/hour

Atmosphere: Wet N<sub>2</sub> gas

25 Oxygen partial pressure: 10<sup>-6</sup> atm

Note that for wetting the atmospheric gas at the time of the processing to remove the binder, firing, and annealing, use was made of a wetter with a water temperature of 35°C.

30 [0101]

External Electrodes

The external electrodes were formed by polishing the end faces of the fired body by sandblasting, then transferring the above external electrode paste on the end  
35 faces and firing in a wet N<sub>2</sub>+H<sub>2</sub> atmosphere at 800°C for 10

minutes.

[0102]

The size of each of the obtained samples was 3.2 mm x 1.6 mm x 1.4 mm. The number of dielectric layers sandwiched between the internal electrode layers was four, the thickness was 3  $\mu\text{m}$ , and the thickness of the internal electrode layers was 1.3  $\mu\text{m}$ .

[0103]

Further, disk-shaped samples were also prepared in addition to the samples of the capacitors. The disk-shaped samples had the same compositions as the dielectric layers of the samples of the capacitors and the same firing conditions and had In-Ga electrodes of diameters of 5 mm coated on the two surfaces of the samples.

[0104]

Each of the samples was evaluated for the following properties:

Specific Dielectric Constant ( $\epsilon_r$ )

The disk-shaped sample was measured for capacity at 25°C by an LCR meter under conditions of 1 kHz and 1V rms. The specific dielectric constant was calculated from the capacity, electrode dimensions, and thickness of the sample. The results are shown in Table 2. The higher the specific dielectric constant, the better.

[0105]

Insulation Resistance (IR)

Each sample of the capacitor was measured for specific resistance at 25°C. The specific resistance was measured by an insulation resistance meter (R8340A (50V-1 minute value) made by Advantest Co.) The results are shown in Table 2. The higher the insulation resistance, the better. Note that the CR product in Table 2 is the product of the dielectric constant and the insulation resistance. Further, the higher the CR product, the better.

[0106]



### Breakdown Voltage (VB)

The breakdown voltage was found by applying a DC voltage to the sample of the multilayer ceramic capacitor at a speed of voltage rise of 100V/second and measuring the voltage when a leakage current of 100 mA was observed. The results are shown in Table 2. The higher the breakdown voltage, the better.

[0107]

### IR Lifetime Under DC Electric Field (High Temperature Accelerated Lifetime, shown as HALT in table)

Each sample of the multilayer ceramic capacitor was subjected to an acceleration test at 180°C under an electric field of 10V/ $\mu$ m. The time until the insulation resistance (IR) became less than  $2 \times 10^5 \Omega$  was used as the lifetime. The results are shown in Table 2. The longer the lifetime, the more improved the durability of the capacitor.

[0108]

### Temperature Characteristic of Capacity (TCC in Table)

Each sample of the multilayer ceramic capacitor was measured for capacity at a temperature range of -55 to 125°C to examine if the X7R characteristic was satisfied. Note that the measurement was conducted using an LCR meter at a measurement voltage of 1V. It was examined if the rate of change of the capacity satisfied the requirement of being within  $\pm 15\%$  (reference temperature of 25°C). When satisfying it, it was indicated as "Good", while when not satisfying it, it was indicated as "Poor".

[0109]

For the B characteristic, the capacity was measured by an LCR meter at a measurement voltage of 1 for -25 to 85°C. It was examined if the rate of change of the capacity satisfied the requirement of being within  $\pm 10\%$  (reference temperature of 20°C). When satisfying it, it was indicated as "Good", while when not satisfying it, it was indicated as "Poor".

[0110]

Change of Capacity Over Time Under DC Electric Field

A DC electric field of 2.5V per  $1\mu\text{m}$  thickness of the dielectric layer was applied to a sample of the multilayer ceramic capacitor (7.5V voltage applied to sample) at  $40^\circ\text{C}$  for 100 hours, then the sample was allowed to stand in a no load state at room temperature for 24 hours and the capacity was measured. The amount of change  $\Delta C$  from the capacity  $C_0$  before application of the DC electric field (initial capacity) was found and the rate of change  $\Delta C/C_0$  was calculated. Note that the capacity was measured under the following conditions.

[0111]

Resistance to Capacity Drop Under DC Bias (DC-Bias Characteristic)

The electrostatic capacity was measured by an LCR meter at room temperature while applying a DC electric field of 0 to  $13\text{V}/\mu\text{m}$  and the electric field when the capacity under the DC electric field became -50% was found. It is preferable that it be at least  $6.3\text{V}/\mu\text{m}$ , if possible at least  $6.5\text{V}/\mu\text{m}$ .

Table 1

Sample No.	Composition at time of calcination (mol)									Cal. temp.
	Main comp. BaTiO <sub>3</sub>	1st sub-comp.		3rd sub-comp. V <sub>2</sub> O <sub>5</sub>	4th subcomp. R alone/no. of moles		5th sub-comp. MnO	Formula (1)	Formula (2)	Tl (°C)
A1	100	2.1	MgO					1.021	0.9794	500
A2	100	2.1	MgO					1.021	0.9794	600
A3	100	2.1	MgO					1.021	0.9794	700
A4	100	2.1	MgO					1.021	0.9794	800
A5	100	2.1	MgO					1.021	0.9794	900
A6	100	2.1	MgO					1.021	0.9794	1000
A7	100	2.1	MgO					1.021	0.9794	1100
A8	100	2.1	MgO					1.021	0.9794	1200
A9	100	2.1	MgO					1.021	0.9794	1300
A10	100	2.1	MgO					1.021	0.9794	1350
A11 (Comp. Ex. 1)										None
B1	100	2.1	CaO					1.021	0.9794	1000
B2	100	2.1	BaO					1.021	0.9794	1000
C1	100	2.1	MgO		4.2	Y		0.9798	1.0206	700
C2	100	2.1	MgO		4.2	Y		0.9798	1.0206	800
C3	100	2.1	MgO		4.2	Y		0.9798	1.0206	900
C4	100	2.1	MgO		4.2	Y		0.9798	1.0206	1000
C5	100	2.1	MgO		4.2	Y		0.9798	1.0206	1100
C6	100	2.1	MgO		4.2	Y	0.375	0.9798	1.0206	700
C7	100	2.1	MgO		4.2	Y	0.375	0.9798	1.0206	800
C8	100	2.1	MgO		4.2	Y	0.375	0.9798	1.0206	900
C9	100	2.1	MgO		4.2	Y	0.375	0.9798	1.0206	1000
C10	100	2.1	MgO		4.2	Y	0.375	0.9798	1.0206	1100
D1	100	2.1	MgO	0.01	4.2	Y	0.375	0.9798	1.0206	500
D2	100	2.1	MgO	0.01	4.2	Y	0.375	0.9798	1.0206	600
D3	100	2.1	MgO	0.01	4.2	Y	0.375	0.9798	1.0206	700
D4	100	2.1	MgO	0.01	4.2	Y	0.375	0.9798	1.0206	800
D5	100	2.1	MgO	0.01	4.2	Y	0.375	0.9798	1.0206	900
D6	100	2.1	MgO	0.01	4.2	Y	0.375	0.9798	1.0206	1000
D7	100	2.1	MgO	0.01	4.2	Y	0.375	0.9798	1.0206	1100
D8	100	2.1	MgO	0.01	4.2	Y	0.375	0.9798	1.0206	1200
D9	100	2.1	MgO	0.01	4.2	Y	0.375	0.9798	1.0206	1300
E1	100	2.1	MgO	0.01	4.2	Dy	0.375	0.9798	1.0206	800
E2	100	2.1	MgO	0.01	4.2	Ho	0.375	0.9798	1.0206	800
E3	100	2.5	MgO	0.01	3.0	Eu	0.375	0.9951	1.0049	800
E4 (Comp. Ex. 2)						Gd				None
E5	100	2.5	MgO	0.01	3.0	Gd	0.375	0.9951	1.0049	800
E6 (Comp. Ex. 3)						Tb				None
E7	100	2.5	MgO	0.01	2.8	Tb	0.375	0.9971	1.0029	800

Notes: The first and fourth subcomponents are calculated as atomic%.

Formula (1): (Ba+first subcomponent)/(Ti+fourth subcomponent)

Formula (2): (Ba+fourth subcomponent)/(Ti+first subcomponent)

[0113]

Table 2

Sample no.	Composition of components additionally added at time of making coating (mol)							TCC	HALT (hr)				er	IR	CR product	Change in capacity over time (t)	DC-bias capacity halving field (V/ $\mu$ m)	VB (V)
	Main comp. BaTiO <sub>3</sub>	1st sub-comp. MgO	4th sub-comp. No. of moles of Y	5th sub-comp. MnO	3rd sub-comp. V <sub>2</sub> O <sub>5</sub>	2nd sub-comp. BaCaSiO <sub>3</sub>	$\Delta C$ -55 (%)		$\Delta C$ +85 (%)	$\Delta C$ +125 (%)	B- char.	X7R						
A1			4.2	0.375	0.01	3	2.2	-7.5	-12.0	-12.0	Good	Good	2370	2.3E+13	4824.1	-5.4	6.5	412
A2			4.2	0.375	0.01	3	1.5	-7.0	-10.3	-10.3	Good	Good	2372	2.3E+13	4828.2	-5.5	6.6	422
A3			4.2	0.375	0.01	3	0.8	-7.3	-8.8	-8.8	Good	Good	2374	2.4E+13	5042.4	-5.1	6.8	453
A4			4.2	0.375	0.01	3	0.5	-7.0	-8.8	-8.8	Good	Good	2374	2.4E+13	5042.4	-4.5	7.0	464
A5			4.2	0.375	0.01	3	0.3	-6.9	-9.9	-9.9	Good	Good	2372	2.5E+13	5248	-4.0	7.2	461
A6			4.2	0.375	0.01	3	-0.7	-7.1	-10.8	-10.8	Good	Good	2370	2.6E+13	5453	-4.0	6.8	455
A7			4.2	0.375	0.01	3	-1.4	-7.7	-11.3	-11.3	Good	Good	2368	2.8E+13	5459	-3.7	6.6	435
A8			4.2	0.375	0.01	3	-2.3	-8.3	-12.6	-12.6	Good	Good	2361	3.1E+13	5851	-3.7	6.6	406
A9			4.2	0.375	0.01	3	-2.9	-10.0	-13.8	-13.8	Good	Good	2359	3.1E+13	6472	-4.0	6.4	396
A10			4.2	0.375	0.01	3	-3.9	-10.0	-14.9	-14.9	Good	Good	2357	3.1E+13	6466	-4.3	6.2	380
A11 (C.E.1)	100	2.1	4.2	0.375	0.01	3	2.8	-7.5	-12.3	-12.3	Good	Good	2368	2.3E+13	4820	-5.5	6.5	381
B1			4.2	0.375	0.01	3	-2.4	-3.4	-6.5	-6.5	Good	Good	2605	2.6E+13	5994	-5.9	6.4	352
B2			4.2	0.375	0.01	3	-3.6	-5.3	-7.0	-7.0	Good	Good	2633	2.4E+13	5592	-6.1	6.3	346
C1				0.375	0.01	3	1.1	-6.8	-10.6	-10.6	Good	Good	2375	3.3E+13	6936	-5.3	6.9	488
C2				0.375	0.01	3	0.6	-6.5	-10.6	-10.6	Good	Good	2380	3.7E+13	7793	-4.1	7.1	501
C3				0.375	0.01	3	0.3	-6.2	-10.4	-10.4	Good	Good	2381	4.2E+13	8850	-3.9	7.3	506
C4				0.375	0.01	3	-0.7	-6.4	-10.7	-10.7	Good	Good	2374	4.2E+13	8624	-4.0	7.2	486
C5				0.375	0.01	3	-1.3	-7.0	-11.8	-11.8	Good	Good	2310	4.2E+13	8586	-3.8	6.8	472
C6					0.01	3	0.9	-6.8	-10.5	-10.5	Good	Good	2369	3.5E+13	7338	-4.6	6.9	490
C7					0.01	3	0.6	-6.2	-10.4	-10.4	Good	Good	2377	4.2E+13	8835	-4.1	7.2	505
C8					0.01	3	0.3	-6.3	-10.3	-10.3	Good	Good	2378	4.2E+13	8839	-3.9	7.5	512
C9					0.01	3	-0.2	-6.4	-10.7	-10.7	Good	Good	2361	4.3E+13	8985	-3.9	7.1	500
C10					0.01	3	-1.1	-6.9	-11.5	-11.5	Good	Good	2305	4.5E+13	9180	-3.7	6.9	496
D1						3	1.6	-7.2	-12.0	-12.0	Good	Good	2366	2.8E+13	5863	-5.0	6.6	392
D2						3	1.3	-7.1	-11.4	-11.4	Good	Good	2372	3.1E+13	6508	-4.8	6.8	422
D3						3	0.8	-6.7	-10.8	-10.8	Good	Good	2375	3.7E+13	7777	-4.4	7.1	498
D4						3	0.6	-6.4	-10.2	-10.2	Good	Good	2381	4.2E+13	8850	-4.0	7.6	500
D5						3	0.3	-6.3	-10.3	-10.3	Good	Good	2380	4.2E+13	8846	-3.8	7.5	512
D6						3	0.4	-6.4	-10.7	-10.7	Good	Good	2349	4.3E+13	8939	-3.8	7.4	500
D7						3	0.4	-6.8	-11.4	-11.4	Good	Good	2333	4.3E+13	8878	-3.9	7.0	492
D8						3	0.8	-7.0	-12.0	-12.0	Good	Good	2301	4.5E+13	9164	-4.1	6.7	485
D9						3	0.6	-7.4	-12.5	-12.5	Good	Good	2296	4.5E+13	9144	-4.5	6.3	383
E1						3	-0.2	-9.9	-14.7	-14.7	Good	Good	2734	4.1E+13	9920	-3.9	6.7	422
E2						3	0.5	-8.4	-13.2	-13.2	Good	Good	2237	4.2E+13	8315	-4.2	7.4	445
E3						3	0.6	22.0	-33.2	-33.2	Poor	Poor	3449	3.9E+13	11904	-8.6	5.2	221
E4 (C.E.2)	100	2.5	3	0.375	0.01	3	0.5	20.1	-32.5	-32.5	Poor	Poor	3120	4.3E+13	11873	-9.3	5.5	220
E5						3	0.6	18.2	-27.4	-27.4	Poor	Poor	3225	3.7E+13	10560	-6.5	5.7	223
E6 (C.E.3)	100	2.5	2.8	0.375	0.01	3	0.5	17.7	-27.0	-27.0	Poor	Poor	3109	4.5E+13	12382	-7.7	6.6	268
E7						3	0.5	-12.9	-19.2	-19.2	Poor	Poor	2940	4.4E+13	11448	-4.3	6.9	395

### Comparative Example 1

As shown in Table 1 and Table 2, the same procedure was followed as for the sample of Example 1, except for not performing calcination and firing using a mixed powder obtained by adding, to 100 moles of the main component  $\text{BaTiO}_3$ , 2.1 moles, converted to  $\text{MgO}$ , of  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ , 0.375 moles of  $\text{MnCO}_3$ , 3.0 moles of  $(\text{Ba}_{0.6}\text{Ca}_{0.4})\text{SiO}_3$ , 0.01 mole of  $\text{V}_2\text{O}_5$ , and 2.1 moles of  $\text{Y}_2\text{O}_3$ , to prepare a disk-shaped sample and a capacitor of Sample A11. These were tested in the same way as Example 1. The results are shown in Table 2.

[0114]

### Example 2

As shown in Table 1, the same procedure was followed as in Example 1, except for using  $\text{CaO}$  or  $\text{BaO}$  as the first subcomponent and performing the calcination at a temperature of  $1000^\circ\text{C}$ , to prepare disk-shaped samples and capacitors of Sample B1 and B2. These were tested in the same way as Example 1. The results are shown in Table 2.

[0115]

Note that when examining the molar ratio of specific components in the pre-calcination powder of  $(\text{Ba}+\text{Ca})/(\text{Ti}+\text{Y})$ , as shown in Table 1, it was 1.021. Further, when examining the molar ratio  $(\text{Ba}+\text{Y})/(\text{Ti}+\text{Ca})$ , as shown in Table 1, it was 0.9794.

[0116]

### Example 3

As shown in Table 1, the same procedure was followed as in Example 1, except for further adding to the pre-calcination powder 2.1 moles of  $\text{MgO}$  and 2.1 moles of  $\text{Y}_2\text{O}_3$  or further 0.375 mole of  $\text{MnCO}_3$  and performing the calcination at a temperature of  $700$  to  $1100^\circ\text{C}$ , to prepare disk-shaped samples and capacitors of Samples C1 and C10. These were tested in the same way as Example 1. The results are shown in Table 2.

[0117]

Note that when examining the molar ratio of specific components in the pre-calcination powder of  $(\text{Ba}+\text{Mg})/(\text{Ti}+\text{Y})$ , as shown in Table 1, it was 0.9798. Further, when examining the molar ratio  $(\text{Ba}+\text{Y})/(\text{Ti}+\text{Mg})$ , as shown in Table 1, it was 1.0206.

[0118]

#### Example 4

As shown in Table 1, the same procedure was followed as in Example 1, except for further adding to the pre-calcination powder 0.01 mole of  $\text{V}_2\text{O}_5$  as a third subcomponent, 2.1 moles of  $\text{Y}_2\text{O}_3$  as a fourth subcomponent, and 0.375 mole of  $\text{MnCO}_3$  as a fifth subcomponent and performing the calcination at a temperature of 500 to 1300°C, to prepare disk-shaped samples and capacitors of Samples D1 to D9. These were tested in the same way as Example 1. The results are shown in Table 2.

[0119]

Note that when examining the molar ratio of specific components in the pre-calcination powder of  $(\text{Ba}+\text{Mg})/(\text{Ti}+\text{Y})$ , as shown in Table 1, it was 0.9798. Further, when examining the molar ratio  $(\text{Ba}+\text{Y})/(\text{Ti}+\text{Mg})$ , as shown in Table 1, it was 1.0206.

[0120]

#### Example 5

As shown in Table 1, the same procedure was followed as in Example 4, except for, instead of the  $\text{Y}_2\text{O}_3$  of the fourth subcomponent, including  $\text{Dy}_2\text{O}_3$  or  $\text{Ho}_2\text{O}_3$  in the pre-calcination powder in a content of 2.1 moles (number of moles of Dy or Ho of 4.2 moles, same below) and performing the calcination at a temperature of 800°C, to prepare disk-shaped samples and capacitors of Samples E1 and E2. These were tested in the same way as Example 1. The results are shown in Table 2.

[0121]

Note that when examining the molar ratio of specific

components in the pre-calcination powder of (Ba+Mg)/(Ti+Dy or Ho), as shown in Table 1, it was 0.9798. Further, when examining the molar ratio (Ba+Dy or Ho)/(Ti+Mg), as shown in Table 1, it was 1.0206.

5 [0122]

Example 6

As shown in Table 1, the same procedure was followed as in Example 4, except for, instead of the  $Y_2O_3$  of the fourth subcomponent, including  $Eu_2O_3$  in the pre-calcination powder in a content of 1.5 moles (number of moles of Eu of 3.0 moles, same below) and performing the calcination at a temperature of 800°C, to prepare a disk-shaped sample and capacitor of Sample E3. These were tested in the same way as Example 1. The results are shown in Table 2.

15 [0123]

Note that when examining the molar ratio of specific components in the pre-calcination powder of (Ba+Mg)/(Ti+Eu), as shown in Table 1, it was 0.9951. Further, when examining the molar ratio (Ba+Eu)/(Ti+Mg), as shown in Table 1, it was 1.0049.

20 [0124]

Example 7

As shown in Table 1, the same procedure was followed as in Example 4, except for, instead of the  $Y_2O_3$  of the fourth subcomponent, including  $Gd_2O_3$  in the pre-calcination powder in a content of 1.5 moles (number of moles of Gd of 3.0 moles, same below) and performing the calcination at a temperature of 800°C, to prepare a disk-shaped sample and capacitor of Sample E5. These were tested in the same way as Example 1. The results are shown in Table 2.

30 [0125]

Note that when examining the molar ratio of specific components in the pre-calcination powder of (Ba+Mg)/(Ti+Gd), as shown in Table 1, it was 0.9951. Further, when examining the molar ratio (Ba+Gd)/(Ti+Mg), as shown in Table 1, it was

1.0049.

[0126]

Comparative Example 2

As shown in Table 1 and Table 2, the same procedure was followed as for the sample of Example 7, except for not performing calcination and firing using a mixed powder obtained by adding, to 100 moles of the main component  $\text{BaTiO}_3$ , 2.5 moles, converted to  $\text{MgO}$ , of  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ , 0.375 mole of  $\text{MnCO}_3$ , 3.0 moles of  $(\text{Ba}_{0.6}\text{Ca}_{0.4})\text{SiO}_3$ , 0.01 mole of  $\text{V}_2\text{O}_5$ , and 1.5 moles of  $\text{Gd}_2\text{O}_3$ , to prepare a disk-shaped sample and a capacitor of Sample E4. These were tested in the same way as Example 7. The results are shown in Table 2.

[0127]

Example 8

As shown in Table 1, the same procedure was followed as in Example 4, except for, instead of the  $\text{Y}_2\text{O}_3$  of the fourth subcomponent, including  $\text{Tb}_4\text{O}_7$  in the pre-calcination powder in a content of 0.7 mole (number of moles of Tb of 2.8 moles, same below) and performing the calcination at a temperature of  $800^\circ\text{C}$ , to prepare a disk-shaped sample and capacitor of Sample E7. These were tested in the same way as Example 4. The results are shown in Table 2.

[0128]

Note that when examining the molar ratio of specific components in the pre-calcination powder of  $(\text{Ba}+\text{Mg})/(\text{Ti}+\text{Tb})$ , as shown in Table 1, it was 0.9971. Further, when examining the molar ratio  $(\text{Ba}+\text{Tb})/(\text{Ti}+\text{Mg})$ , as shown in Table 1, it was 1.0029.

[0129]

Comparative Example 3

As shown in Table 1 and Table 2, the same procedure was followed as for the sample of Example 8, except for not performing calcination and firing using a mixed powder obtained by adding, to 100 moles of the main component  $\text{BaTiO}_3$ , 2.5 moles, converted to  $\text{MgO}$ , of  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ ,



0.375 mole of  $\text{MnCO}_3$ , 3.0 moles of  $(\text{Ba}_{0.6}\text{Ca}_{0.4})\text{SiO}_3$ , 0.01 mole of  $\text{V}_2\text{O}_5$ , and 0.7 mole of  $\text{Tb}_4\text{O}_7$ , to prepare a disk-shaped sample and a capacitor of Sample E6. These were tested in the same way as Example 8. The results are shown in Table 2.

5 [0130]

Example 9

The same procedure was followed as in Example 1, except for including in the pre-calcination powder magnesium carbonate of the moles shown in Table 3, converted to  $\text{MgO}$ ,  
10 with respect to 60 to 80 moles of  $\text{BaTiO}_3$  and additionally adding not calcined main component and subcomponents to the calcined powder to give a wt% of the calcined powder of 60 to 80 wt% as shown in Table 4,  
to prepare disk-shaped samples and capacitors of Sample F1 to F3. These were tested in the same way as Example 1. The results are shown in Table 2.

[0131]

Note that when examining the molar ratio of specific components in the pre-calcination powder of  $(\text{Ba}+\text{Mg})/(\text{Ti}+\text{Y})$ , as shown in Table 1, it was 1.021. Further, when examining the molar ratio  $(\text{Ba}+\text{Y})/(\text{Ti}+\text{Mg})$ , as shown in Table 1, it was 0.9794.

Table 3

Sample no.	Composition at time of calcination (mol)							Cal. temp.	
	Main comp. BaTiO <sub>3</sub>	1st subcomp.		3rd sub-comp. V <sub>2</sub> O <sub>5</sub>	4th subcomp. No. of moles of R alone	5th sub-comp. MnO	Formula (1)		Formula (2)
F1	60	1.26	MgO				1.021	0.9794	1000
F2	70	1.47	MgO				1.021	0.9794	1000
F3	80	1.68	MgO				1.021	0.9794	1000
G1	100	2.1	MgO	4.2	Y	0.375	0.9798	1.0206	900
G2	100	2.1	MgO	4.2	Y	0.375	0.9798	1.0206	900
G3	100	2.1	MgO	4.2	Y	0.375	0.9798	1.0206	900
G4	100	2.1	MgO	4.2	Y	0.375	0.9798	1.0206	900
H1	100	2.1	MgO	4.2	Y	0.375	0.9798	1.0206	900
H2	100	2.1	MgO	4.2	Y	0.375	0.9798	1.0206	900
H3	100	2.1	MgO	4.2	Y	0.375	0.9798	1.0206	900

Notes: The first and fourth subcomponents are calculated as atomic%.

Formula (1):  $(\text{Ba} + \text{first subcomponent}) / (\text{Ti} + \text{fourth subcomponent})$

Formula (2):  $(\text{Ba} + \text{fourth subcomponent}) / (\text{Ti} + \text{first subcomponent})$

Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100
1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	

Sample no.	Composition of components additionally added at time of making coating (mol)										TCC	HALT (hr)	er	IR	CR product	Change of capacity over time (%)	DC-bias capacity halving field (V/ $\mu$ m)	VB (V)		
	Composition of components additionally added at time of making coating (mol)							Cal-cined comp. wt%	2nd sub-comp. (BaCa)SiO <sub>3</sub>	3rd sub-comp. V <sub>2</sub> O <sub>5</sub>									5th sub-comp. MnO	4th sub-comp. No. of moles of Y
	Main comp. BaTiO <sub>3</sub>	1st sub-comp. MgO	4th sub-comp. No. of moles of Y	5th sub-comp. MnO	3rd sub-comp. V <sub>2</sub> O <sub>5</sub>	2nd sub-comp. (BaCa)SiO <sub>3</sub>	Cal-cined comp. wt%													
F1	40	0.84	4.2	0.375	0.01	3	60	2.6	-7.5	-12.3	Good	22.0	2374	2.3E+13	4832	-5.3	6.5	360		
F2	30	0.63	4.2	0.375	0.01	3	70	1.8	-7.5	-12.0	Good	25.0	2374	2.3E+13	4832	-4.3	6.7	383		
F3	20	0.42	4.2	0.375	0.01	3	80	0.9	-7.2	-11.7	Good	27.9	2380	2.9E+13	6108	-4.6	6.9	403		
G1	0					3	100	0.5	-6.2	-9.7	Good	71.4	2385	1.1E+13	2322	-3.8	7.5	488		
G2	0					3	100	0.5	-6.2	-9.4	Good	88.5	2410	7.5E+12	1600	-3.6	7.4	465		
G3	0					3	100	0.7	-5.9	-8.7	Good	105.0	2413	2.0E+12	427	-3.6	7.4	462		
G4	0					3	100	0.6	-4.2	-7.1	Good	153.0	2377	8.7E+11	183	-3.9	7.1	411		
H1	0					3(*1)	100	0.4	-6.5	-11.5	Good	60.5	2374	3.8E+13	7984	-3.8	7.3	430		
H2	0					3(*2)	100	0.6	-7.4	-11.9	Good	46.3	2370	4.0E+13	8390	-3.8	7.3	440		
H3	0					3(*3)	100	0.5	-6.3	-9.3	Good	101.6	2303	2.0E+12	408	-3.9	7.0	400		

\*3:  $\text{Li}_2\text{O-BaO-SiO}_2$  (4:2:4)

#### Example 10

As shown in Table 3, the same procedure was followed as with Sample D5 of Example 4, except for changing the number of moles of  $V_2O_5$  of the third subcomponent in the pre-calcination powder in the range of 0.05 to 0.5, to prepare disk-shaped samples and capacitors of Samples G1 to G4. These were tested in the same way as Example 4. The results are shown in Table 4.

[0134]

Note that when examining the molar ratio of specific components in the pre-calcination powder of  $(Ba+Mg)/(Ti+Y)$ , as shown in Table 3, it was 0.9798. Further, when examining the molar ratio  $(Ba+Y)/(Ti+Mg)$ , as shown in Table 3, it was 1.0206.

[0135]

#### Example 11

The same procedure was followed as with Sample D5 of Example 4, except for making the number of moles of the  $V_2O_5$  of the third subcomponent in the pre-calcination powder 0.01 or 0.1 and using a second subcomponent additionally added after calcination of the following composition, to prepare disk-shaped samples and capacitors of Samples H1 to H3. These were tested in the same way as Example 4. In Samples H1 and H3, as the second subcomponent, 3.0 moles of a mixed powder of  $Li_2O-BaO-SiO_2$  (molar ratio: 2:4:4 or 4:2:4) was used. In Sample H2, as the second subcomponent, 3.0 moles of a mixed powder of  $B_2O_3-BaO-SiO_2$  (molar ratio: 1:4.5:4.5) was used.

[0136]

Note that when examining the molar ratio of specific components in the pre-calcination powder of  $(Ba+Mg)/(Ti+Y)$ , as shown in Table 3, it was 0.9798. Further, when examining the molar ratio  $(Ba+Y)/(Ti+Mg)$ , as shown in Table 3, it was 1.0206.

[0137]

### Evaluation

As shown in Tables 1 to 4, it could be confirmed that all of the examples of the present invention could satisfy the X7R characteristic and B characteristic. Further, when  
5 comparing Comparative Example 1, that is, Sample A11, and the examples of the present invention, that is, Samples A1 to A10, B1, B2, C1 to C10, and D1 to D9, it could be confirmed that the examples of the invention were longer in  
10 HALT (IR lifetime), higher in CR product, smaller in change of electrostatic capacity over time under a DC electric field, and higher in capacity halving field under a DC electric field.

[0138]

Further, when comparing for example the comparative  
5 example of Sample A11 and the examples of the invention of Samples D2 to D5, it could be confirmed that the breakdown voltage could be improved by suitably selecting the composition of the pre-calcination powder and calcination temperature.

[0139]

Further, when examining the results of Samples C1 to C10 and D1 to D9, it could be confirmed that the calcination temperature is preferably from 500°C to less than 1200°C, more preferably 600 to 900°C when the pre-calcination powder  
25 includes the fourth subcomponent. Further, when examining the results of Samples A1 to A10, it could be confirmed that the calcination temperature is preferably 600 to 1300°C, more preferably 900 to 1300°C, still more preferably 1000 to 1200°C when the pre-calcination powder does not include the  
30 material of the fourth subcomponent. In these temperature ranges, the HALT (IR lifetime) was particularly improved.

[0140]

Further, when comparing Samples A1 to A10 and D1 to D9, it could be confirmed that the HALT (IR lifetime) and  
35 breakdown voltage characteristic were particularly improved

under molar ratios of specific components in the pre-calcination powder of a (Ba+metal element of first subcomponent)/(Ti+metal element of fourth subcomponent) of less than 1 and a (Ti+metal element of fourth subcomponent)/(Ba+metal element of first subcomponent) of over 1.

[0141]

Still further, when comparing Samples F1 to F3, it could be confirmed that it is preferable that the pre-calcination powder be at least 60 wt%, more preferably at least 70 wt%, if possible at least 80 wt%, with respect to the dielectric material as a whole as 100 wt%. It could be confirmed that the greater the ratio of the calcined powder, the more improved the properties.

[0142]

Further, when examining the results of Samples E3 to E7, it could be confirmed that even when using a Tb oxide or Gd oxide as the fourth subcomponent, due to the calcination method of the present invention, while the X7R characteristic was not satisfied, the other various properties (in particular the IR lifetime) was improved.

[0143]

Further, when examining Samples G1 to G4 etc., it could be confirmed that by making the ratio of the third subcomponent 0.01 to 0.1 mole, preferably 0.01 to less than 0.1 mole, the insulation resistance (IR), CR product, breakdown voltage (VB) characteristic, and resistance to drop in capacity under DC bias (DC-Bias characteristic) were improved.

[0144]

Further, when examining Samples H1 to H3 etc., it could be confirmed that the effects of the present invention could be obtained even when using SiO<sub>2</sub>, Li<sub>2</sub>O, BaO, etc. as the second subcomponent.

[0145]

While the invention has been described with reference to specific embodiments chosen for purpose of illustration, it should be apparent that numerous modifications could be made thereto by those skilled in the art without departing from  
5 the basic concept and scope of the invention.

11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316 317 318 319 320 321 322 323 324 325 326 327 328 329 330 331 332 333 334 335 336 337 338 339 340 341 342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367 368 369 370 371 372 373 374 375 376 377 378 379 380 381 382 383 384 385 386 387 388 389 390 391 392 393 394 395 396 397 398 399 400 401 402 403 404 405 406 407 408 409 410 411 412 413 414 415 416 417 418 419 420 421 422 423 424 425 426 427 428 429 430 431 432 433 434 435 436 437 438 439 440 441 442 443 444 445 446 447 448 449 450 451 452 453 454 455 456 457 458 459 460 461 462 463 464 465 466 467 468 469 470 471 472 473 474 475 476 477 478 479 480 481 482 483 484 485 486 487 488 489 490 491 492 493 494 495 496 497 498 499 500 501 502 503 504 505 506 507 508 509 510 511 512 513 514 515 516 517 518 519 520 521 522 523 524 525 526 527 528 529 530 531 532 533 534 535 536 537 538 539 540 541 542 543 544 545 546 547 548 549 550 551 552 553 554 555 556 557 558 559 560 561 562 563 564 565 566 567 568 569 570 571 572 573 574 575 576 577 578 579 580 581 582 583 584 585 586 587 588 589 590 591 592 593 594 595 596 597 598 599 600 601 602 603 604 605 606 607 608 609 610 611 612 613 614 615 616 617 618 619 620 621 622 623 624 625 626 627 628 629 630 631 632 633 634 635 636 637 638 639 640 641 642 643 644 645 646 647 648 649 650 651 652 653 654 655 656 657 658 659 660 661 662 663 664 665 666 667 668 669 670 671 672 673 674 675 676 677 678 679 680 681 682 683 684 685 686 687 688 689 690 691 692 693 694 695 696 697 698 699 700 701 702 703 704 705 706 707 708 709 710 711 712 713 714 715 716 717 718 719 720 721 722 723 724 725 726 727 728 729 730 731 732 733 734 735 736 737 738 739 740 741 742 743 744 745 746 747 748 749 750 751 752 753 754 755 756 757 758 759 760 761 762 763 764 765 766 767 768 769 770 771 772 773 774 775 776 777 778 779 780 781 782 783 784 785 786 787 788 789 790 791 792 793 794 795 796 797 798 799 800 801 802 803 804 805 806 807 808 809 810 811 812 813 814 815 816 817 818 819 820 821 822 823 824 825 826 827 828 829 830 831 832 833 834 835 836 837 838 839 840 841 842 843 844 845 846 847 848 849 850 851 852 853 854 855 856 857 858 859 860 861 862 863 864 865 866 867 868 869 870 871 872 873 874 875 876 877 878 879 880 881 882 883 884 885 886 887 888 889 890 891 892 893 894 895 896 897 898 899 900 901 902 903 904 905 906 907 908 909 910 911 912 913 914 915 916 917 918 919 920 921 922 923 924 925 926 927 928 929 930 931 932 933 934 935 936 937 938 939 940 941 942 943 944 945 946 947 948 949 950 951 952 953 954 955 956 957 958 959 960 961 962 963 964 965 966 967 968 969 970 971 972 973 974 975 976 977 978 979 980 981 982 983 984 985 986 987 988 989 990 991 992 993 994 995 996 997 998 999 1000 1001 1002 1003 1004 1005 1006 1007 1008 1009 1010 1011 1012 1013 1014 1015 1016 1017 1018 1019 1020 1021 1022 1023 1024 1025 1026 1027 1028 1029 1030 1031 1032 1033 1034 1035 1036 1037 1038 1039 1040 1041 1042 1043 1044 1045 1046 1047 1048 1049 1050 1051 1052 1053 1054 1055 1056 1057 1058 1059 1060 1061 1062 1063 1064 1065 1066 1067 1068 1069 1070 1071 1072 1073 1074 1075 1076 1077 1078 1079 1080 1081 1082 1083 1084 1085 1086 1087 1088 1089 1090 1091 1092 1093 1094 1095 1096 1097 1098 1099 1100 1101 1102 1103 1104 1105 1106 1107 1108 1109 1110 1111 1112 1113 1114 1115 1116 1117 1118 1119 1120 1121 1122 1123 1124 1125 1126 1127 1128 1129 1130 1131 1132 1133 1134 1135 1136 1137 1138 1139 1140 1141 1142 1143 1144 1145 1146 1147 1148 1149 1150 1151 1152 1153 1154 1155 1156 1157 1158 1159 1160 1161 1162 1163 1164 1165 1166 1167 1168 1169 1170 1171 1172 1173 1174 1175 1176 1177 1178 1179 1180 1181 1182 1183 1184 1185 1186 1187 1188 1189 1190 1191 1192 1193 1194 1195 1196 1197 1198 1199 1200 1201 1202 1203 1204 1205 1206 1207 1208 1209 1210 1211 1212 1213 1214 1215 1216 1217 1218 1219 1220 1221 1222 1223 1224 1225 1226 1227 1228 1229 1230 1231 1232 1233 1234 1235 1236 1237 1238 1239 1240 1241 1242 1243 1244 1245 1246 1247 1248 1249 1250 1251 1252 1253 1254 1255 1256 1257 1258 1259 1260 1261 1262 1263 1264 1265 1266 1267 1268 1269 1270 1271 1272 1273 1274 1275 1276 1277 1278 1279 1280 1281 1282 1283 1284 1285 1286 1287 1288 1289 1290 1291 1292 1293 1294 1295 1296 1297 1298 1299 1300 1301 1302 1303 1304 1305 1306 1307 1308 1309 1310 1311 1312 1313 1314 1315 1316 1317 1318 1319 1320 1321 1322 1323 1324 1325 1326 1327 1328 1329 1330 1331 1332 1333 1334 1335 1336 1337 1338 1339 1340 1341 1342 1343 1344 1345 1346 1347 1348 1349 1350 1351 1352 1353 1354 1355 1356 1357 1358 1359 1360 1361 1362 1363 1364 1365 1366 1367 1368 1369 1370 1371 1372 1373 1374 1375 1376 1377 1378 1379 1380 1381 1382 1383 1384 1385 1386 1387 1388 1389 1390 1391 1392 1393 1394 1395 1396 1397 1398 1399 1400 1401 1402 1403 1404 1405 1406 1407 1408 1409 1410 1411 1412 1413 1414 1415 1416 1417 1418 1419 1420 1421 1422 1423 1424 1425 1426 1427 1428 1429 1430 1431 1432 1433 1434 1435 1436 1437 1438 1439 1440 1441 1442 1443 1444 1445 1446 1447 1448 1449 1450 1451 1452 1453 1454 1455 1456 1457 1458 1459 1460 1461 1462 1463 1464 1465 1466 1467 1468 1469 1470 1471 1472 1473 1474 1475 1476 1477 1478 1479 1480 1481 1482 1483 1484 1485 1486 1487 1488 1489 1490 1491 1492 1493 1494 1495 1496 1497 1498 1499 1500 1501 1502 1503 1504 1505 1506 1507 1508 1509 1510 1511 1512 1513 1514 1515 1516 1517 1518 1519 1520 1521 1522 1523 1524 1525 1526 1527 1528 1529 1530 1531 1532 1533 1534 1535 1536 1537 1538 1539 1540 1541 1542 1543 1544 1545 1546 1547 1548 1549 1550 1551 1552 1553 1554 1555 1556 1557 1558 1559 1560 1561 1562 1563 1564 1565 1566 1567 1568 1569 1570 1571 1572 1573 1574 1575 1576 1577 1578 1579 1580 1581 1582 1583 1584 1585 1586 1587 1588 1589 1590 1591 1592 1593 1594 1595 1596 1597 1598 1599 1600 1601 1602 1603 1604 1605 1606 1607 1608 1609 1610 1611 1612 1613 1614 1615 1616 1617 1618 1619 1620 1621 1622 1623 1624 1625 1626 1627 1628 1629 1630 1631 1632 1633 1634 1635 1636 1637 1638 1639 1640 1641 1642 1643 1644 1645 1646 1647 1648 1649 1650 1651 1652 1653 1654 1655 1656 1657 1658 1659 1660 1661 1662 1663 1664 1665 1666 1667 1668 1669 1670 1671 1672 1673 1674 1675 1676 1677 1678 1679 1680 1681 1682 1683 1684 1685 1686 1687 1688 1689 1690 1691 1692 1693 1694 1695 1696 1697 1698 1699 1700 1701 1702 1703 1704 1705 1706 1707 1708 1709 1710 1711 1712 1713 1714 1715 1716 1717 1718 1719 1720 1721 1722 1723 1724 1725 1726 1727 1728 1729 1730 1731 1732 1733 1734 1735 1736 1737 1738 1739 1740 1741 1742 1743 1744 1745 1746 1747 1748 1749 1750 1751 1752 1753 1754 1755 1756 1757 1758 1759 1760 1761 1762 1763 1764 1765 1766 1767 1768 1769 1770 1771 1772 1773 1774 1775 1776 1777 1778 1779 1780 1781 1782 1783 1784 1785 1786 1787 1788 1789 1790 1791 1792 1793 1794 1795 1796 1797 1798 1799 1800 1801 1802 1803 1804 1805 1806 1807 1808 1809 1810 1811 1812 1813 1814 1815 1816 1817 1818 1819 1820 1821 1822 1823 1824 1825 1826 1827 1828 1829 1830 1831 1832 1833 1834 1835 1836 1837 1838 1839 1840 1841 1842 1843 1844 1845 1846 1847 1848 1849 1850 1851 1852 1853 1854 1855 1856 1857 1858 1859 1860 1861 1862 1863 1864 1865 1866 1867 1868 1869 1870 1871 1872 1873 1874 1875 1876 1877 1878 1879 1880 1881 1882 1883 1884 1885 1886 1887 1888 1889 1890 1891 1892 1893 1894 1895 1896 1897 1898 1899 1900 1901 1902 1903 1904 1905 1906 1907 1908 1909 1910 1911 1912 1913 1914 1915 1916 1917 1918 1919 1920 1921 1922 1923 1924 1925 1926 1927 1928 1929 1930 1931 1932 1933 1934 1935 1936 1937 1938 1939 1940 1941 1942 1943 1944 1945 1946 1947 1948 1949 1950 1951 1952 1953 1954 1955 1956 1957 1958 1959 1960 1961 1962 1963 1964 1965 1966 1967 1968 1969 1970 1971 1972 1973 1974 1975 1976 1977 1978 1979 1980 1981 1982 1983 1984 1985 1986 1987 1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023 2024 2025 2026 2027 2028 2029 2030 2031 2032 2033 2034 2035 2036 2037 2038 2039 2040 2041 2042 2043 2044 2045 2046 2047 2048 2049 2050 2051 2052 2053 2054 2055 2056 2057 2058 2059 2060 2061 2062 2063 2064 2065 2066 2067 2068 2069 2070 2071 2072 2073 2074 2075 2076 2077 2078 2079 2080 2081 2082 2083 2084 2085 2086 2087 2088 2089 2090 2091 2092 2093 2094 2095 2096 2097 2098 2099 2100 2101 2102 2103 2104 2105 2106 2107 2108 2109 2110 2111 2112 2113 2114 2115 2116 2117 2118 2119 2120 2121 2122 2123 2124 2125 2126 2127 2128 2129 2130 2131 2132 2133 2134 2135 2136 2137 2138 2139 2140 2141 2142 2143 2144 2145 2146 2147 2148 2149 2150 2151 2152 2153 2154 2155 2156 2157 2158 2159 2160 2161 2162 2163 2164 2165 2166 2167 2168 2169 2170 2171 2172 2173 2174 2175 2176 2177 2178 2179 2180 2181 2182 2183 2184 2185 2186 2187 2188 2189 2190 2191 2192 2193 2194 2195 2196 2197 2198 2199 2200 2201 2202 2203 2204 2205 2206 2207 2208 2209 2210 2211 2212 2213 2214 2215 2216 2217 2218 2219 2220 2221 2222 2223 2224 2225 2226 2227 2228 2229 2230 2231 2232 2233 2234 2235 2236 2237 2238 2239 2240 2241 2242 2243 2244 2245 2246 2247 2248 2249 2250 2251 2252 2253 2254 2255 2256 2257 2258 2259 2260 2261 2262 2263 2264 2265 2266 2267 2268 2269 2270 2271 2272 2273 2274 2275 2276 2277 2278 2279 2280 2281 2282 2283 2284 2285 2286 2287 2288 2289 2290 2291 2292 2293 2294 2295 2296 2297 2298 2299 2300 2301 2302 2303 2304 2305 2306 2307 2308 2309 2310 2311 2312 2313 2314 2315 2316 2317 2318 2319 2320 2321 2322 2323 2324 2325 2326 2327 2328 2329 2330 2331 2332 2333 2334 2335 2336 2337 2338 2339 2340 2341 2342 2343 2344 2345 2346 2347 2348 2349 2350 2351 2352 2353 2354 2355 2356 2357 2358 2359 2360 2361 2362 2363 2364 2365 2366 2367 2368 2369 2370 2371 2372 2373 2374 2375 2376 2377 2378 2379 2380 2381 2382 2383 2384 2385 2386 2387 2388 2389 2390 2391 2392 2393 2394 2395 2396 2397 2398 2399 2400 2401 2402 2403 2404 2405 2406 2407 2408 2409 2410 2411 2412 2413 2414 2415 2416 2417 2418 2419 2420 2421 2422 2423 2424 2425 2426 2427 2428 2429 2430 2431 2432 2433 2434 2435 2436 2437 2438 2439 2440 2441 2442 2443 2444 2445 2446 2447 2448 2449 2450 2451 2452 2453 2454 2455 2456 2457 2458 2459 2460 2461 2462 2463 2464 2465 2466 2467 2468 2469 2470 2471 2472 2473 2474 2475 2476 2477 2478 2479 2480 2481 2482 2483 2484 2485 2486 2487 2488 2489 2490 2491 2492 2493 2494 2495 2496 2497 2498 2499 2500 2501 2502 2503 2504 2505 2506 2507 2508 2509 2510 2511 2512 2513 2514 2515 2516 2517 2518 2519 2520 2521 2522 2523 2524 2525 2526 2527 2528 2529 2530 2531 2532 2533 2534 2535 2536 2537 2538 2539 2540 2541 2542 2543 2544 2545 2546 2547 2548 2549 2550 2551 2552 2553 2554 2555 2556 2557 2558 2559 2560 2561 2562 2563 2564 2565 2566 2567 2568 2569 2570 2571 2572 2573 2574 2575 2576 2577 2578 2579 2580 2581 2582 2583 2584 2585 2586 2587 2588 2589 2590 2591 2592 2593 2594 2595 2596 2597 2598 2599 2600 2601 2602 2603 2604 2605 2606 2607 2608 2609 2610 2611 2612 2613 2614 2615 2616 2617 2618 2619 2620 2621 2622 2623 2624 2625 2626 2627 2628 2629 2630 2631 2632 2633 2634 2635 2636 2637 2638 2639 2640 2641 2642 2643 2644 2645 2646 2647 2648 2649 2650 2651 2652 2653 2654 2655 2656 2657 2658 2659 2660 2661 2662 2663 2664 2665 2666 2667 2668 2669 2670 2671 2672 2673 2674 2675 2676 2677 2678 2679 2680 2681